

Restoring the Pauli principle in the random phase approximation ground state

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Random phase approximation ground state contains electronic configurations where two (and more) identical electrons can occupy the same molecular spin-orbital in apparent violation of the Pauli exclusion principle. This unphysical overcounting of electronic configurations happens due to quasiboson approximation in the treatment of electron-hole pair creation and annihilation operators. We describe the method to restore the Pauli principle in the random phase approximation wavefunction and obtain the corrections to expressions for molecular observables. The proposed theory is illustrated by the calculations of molecular dipole moments. The corrected for the Pauli principle Hartree-Fock based RPA gives the results of comparable accuracy with Møller-Plesset second order perturbation theory and coupled-cluster singles and doubles method, while standard RPA significantly overestimates the role electronic correlations.

I. INTRODUCTION

Random phase approximation (RPA) has recently emerged as a very promising method to study correlated ground states in molecules.^{1–8} RPA calculations, especially when they are performed based on the density functional theory, give accurate total molecular correlation energies, reaction barriers, electron affinities, ionisation potentials^{1–7,9–11} and provides physically correct description of van der Waals intermolecular interactions.^{12–14} The connection of RPA with the coupled-cluster doubles approach as been recently established,^{2,15} which puts the method into the context of traditional quantum chemistry practices.

In this paper we would like to draw the attention to the problem of violation of the Pauli exclusion principle in the RPA ground state and discuss the way of correcting it. Although this problem has been known in nuclear physics since 1968¹⁶ and, since then, has been a subject of intensive studies there,^{17–19} it has not yet received a proper consideration in quantum chemical community. To understand the problem let us look at the (schematically written) RPA ground state wavefunction^{20,21}

$$|\Psi_0\rangle \sim e^{\sum T_{p_1 h_1 p_2 h_2} c_{p_1}^\dagger c_{h_1} c_{p_2}^\dagger c_{h_2}} |HF\rangle. \quad (1)$$

Here and throughout the paper, indices h and p refer to Hartree-Fock occupied and virtual molecular orbitals, respectively, and $c_k^\dagger(c_k)$ creates (annihilates) an electron in the Hartree-Fock molecular orbital k . $|HF\rangle$ is the Hartree-Fock ground state vector. The spin index is suppressed in the introduction for the simplicity. RPA treats particle-hole pair creation operators $c_p^\dagger c_h$ as bosons approximating the commutator (so-called quasiboson approximation^{20,21}) as

$$[c_{p_1}^\dagger c_{h_1}, c_{p_2}^\dagger c_{h_2}] \approx \delta_{p_1 p_2} \delta_{h_1 h_2}, \quad (2)$$

and therefore neglecting the internal fermionic structure of these operators. This leads to the over-counting of the configurations in the RPA ground state wavefunction (the configurations with $p_1 = p_2$ and $h_1 = h_2$ in the exponent (1), which otherwise would be forbidden by the

Pauli principle, do contribute to the RPA ground state). The violation of the Pauli principle is amplified in the RPA due to the exponential structure of the ground state – expanding the exponent we see that terms containing two, four, six, eight and more identical electrons are allowed to occupy the same single-particle state. Therefore, the RPA ground state wavefunction (if it is treated in quasiboson approximation) over-correlates the electronic systems by including unphysical configurations and by letting the electrons to come closer in the violation of the Pauli principle.

How to remove these unphysical states from the RPA ground state wavefunction and restore the Pauli principle? How to correct for the Pauli principle the final expression for computed observables and at the same time preserve the original RPA equations? These are the questions which interest us in this paper.

II. THEORY

A. RPA ground state vector with the Pauli principle corrections

We will work with the Hartree-Fock quasiparticle creation and annihilation operators, $a_{k\sigma}^\dagger$ and $a_{k\sigma}$, which are related to the original electron creation and annihilation operators on the Hartree-Fock spin-orbital, $c_{k\sigma}^\dagger$ and $c_{k\sigma}$, via the transformations

$$a_{k\sigma}^\dagger = \begin{cases} c_{k\sigma}^\dagger, & \text{if } k \text{ is virtual orbital,} \\ c_{k\sigma}, & \text{if } k \text{ is occupied orbital,} \end{cases} \quad (3)$$

and

$$a_{k\sigma} = \begin{cases} c_{k\sigma}, & \text{if } k \text{ is virtual orbital,} \\ c_{k\sigma}^\dagger, & \text{if } k \text{ is occupied orbital.} \end{cases} \quad (4)$$

Here $\sigma = -1/2, 1/2$ are two projections of electron spin. The quasiparticle operators defined above have Hartree-Fock ground state $|HF\rangle$ as a vacuum

$$a_{k\sigma}|HF\rangle = 0 \text{ for all } k, \sigma. \quad (5)$$

The building blocks for the RPA wavefunction are the particle-hole pair creation operators $C_{ph}^\dagger(JM)$ defined as

$$C_{ph}^\dagger(JM) = \sum_{\sigma\sigma'} \langle \frac{1}{2}\sigma \frac{1}{2}\sigma' | JM \rangle a_{p\sigma}^\dagger a_{h\sigma'}^\dagger. \quad (6)$$

It creates the particle-hole excited pair with spin J and spin projection M . Over-line over spin indices means angular momentum time-reversal state $C_{ph}^\dagger(\overline{JM}) = (-1)^{J+M} C_{ph}^\dagger(J-M)$ and $a_{h\sigma}^\dagger = (-1)^{1/2+\sigma} a_{h-\sigma}^\dagger$. The Clebsch-Gordan coefficient $\langle \frac{1}{2}\sigma \frac{1}{2}\sigma' | JM \rangle$ couples electronic spins of occupied and virtual molecular orbitals into singlet $J = 0, M = 0$ or triplet $J = 1, M = -1, 0, 1$ states.

The RPA ground state wavefunction has the following form^{20,21}

$$|\Psi_0\rangle = Ne^S|HF\rangle, \quad (7)$$

where

$$S = \frac{1}{2} \sum_{JM} \sum_{ph p'h'} T_{ph p'h'}^J C_{ph}^\dagger(JM) C_{p'h'}^\dagger(\overline{JM}). \quad (8)$$

Here and everywhere in the paper

$$\sum_{JM} = \sum_{J=0}^1 \sum_{M=-J}^J. \quad (9)$$

The correlated RPA ground state $|\Psi_0\rangle$ is a vacuum for the RPA excitation annihilation operators

$$Q_{JMi}|\Psi_0\rangle = 0, \text{ for all } J, M, \text{ and } i, \quad (10)$$

where the excitation annihilation operator is obtained from the corresponding creation operator

$$Q_{JMi}^\dagger = \sum_{ph} X_{ph}^{Ji} C_{ph}^\dagger(JM) - Y_{ph}^{Ji} C_{ph}^\dagger(\overline{JM}) \quad (11)$$

via Hermitian conjugation.

The structure of operator Q_{JMi}^\dagger and related RPA excitation energy ω_{Ji} are determined from the standard

system of RPA equation, which we write separately for singlet ($J = 0$) and triplet ($J = 1$) electronic excitations

$$\sum_{p'h'} A_{ph,p'h'}^J X_{p'h'}^{Ji} + B_{ph,p'h'}^J Y_{p'h'}^{Ji} = \omega_{Ji} X_{ph}^{Ji}, \quad (12)$$

$$\sum_{p'h'} B_{ph,p'h'}^J X_{p'h'}^{Ji} + A_{ph,p'h'}^J Y_{p'h'}^{Ji} = -\omega_{Ji} Y_{ph}^{Ji}. \quad (13)$$

Matrices A and B are given by the following expressions

$$A_{ph,p'h'}^J = (\epsilon_p - \epsilon_h) \delta_{pp'} \delta_{hh'} + [1 + (-1)^J] (ph|p'h') - (hh'|p'p), \quad (14)$$

$$B_{ph,p'h'}^J = [1 + (-1)^J] (ph|p'h') - (p'h|ph'), \quad (15)$$

where ϵ_k is Hartree-Fock energy of k molecular orbital and $(kl|mn)$ is a two-electron integral in the Mulliken notations.

Suppose that we know X_{ph}^{Ji} and Y_{ph}^{Ji} in (11) from the solution of the RPA equations. Our goal in this section is to solve (10) directly and determine coefficient T without the use of the quasiboson approximation (2). We rewrite (10) as

$$Q_{JMi} e^S |HF\rangle = 0 \quad (16)$$

Using the standard operator identity we get

$$e^S (Q_{JMi} + [Q_{JMi}, S] + \frac{1}{2!} [[Q_{JMi}, S], S] + \dots) |HF\rangle = 0. \quad (17)$$

We neglect higher order terms $O(S^2)$ in this expansion and the equation for operator S becomes

$$(Q_{JMi} + [Q_{JMi}, S]) |HF\rangle = 0. \quad (18)$$

Substituting explicit expression for Q_{JMi} into (18) and rearranging the terms, we get

$$\frac{1}{2} \sum_{JM} \sum_{p_1 h_1 p_2 h_2} \sum_{p_3 h_3} T_{p_1 h_1 p_2 h_2}^J X_{p_3 h_3}^{J_3 i} \left[C_{p_3 h_3}(J_3 M_3), C_{p_1 h_1}^\dagger(JM) C_{p_2 h_2}^\dagger(\overline{JM}) \right] |HF\rangle = \sum_{p_3 h_3} Y_{p_3 h_3}^{J_3 i} C_{p_3 h_3}^\dagger(\overline{J_3 M_3}) |HF\rangle. \quad (19)$$

The commutator in the l.h.s. of (19) can be exactly computed and (19) becomes

$$\begin{aligned}
& \sum_{JM} \sum_{p_1 h_1 p_2 h_2} \sum_{p_3 h_3} T_{p_1 h_1 p_2 h_2}^J X_{p_3 h_3}^{J_3 i} \left\{ \delta_{JJ_3} \delta_{MM_3} \delta_{p_1 p_3} \delta_{h_1 h_3} \right. \\
& - \frac{1}{2} \sum_{\sigma_3 \sigma'_3 \sigma_1 \sigma'_1} \langle \frac{1}{2} \sigma_3 \frac{1}{2} \sigma'_3 | J_3 M_3 \rangle \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | JM \rangle \left(\delta_{p_3 p_1} \delta_{\sigma_3 \sigma_1} a_{h_1 \sigma'_1}^\dagger a_{h_3 \sigma'_3} + \delta_{h_3 h_1} \delta_{\sigma'_3 \sigma'_1} a_{p_1 \sigma_1}^\dagger a_{p_3 \sigma_3} \right) \left. \right\} C_{p_2 h_2}^\dagger (\overline{JM}) |HF\rangle \\
& = \sum_{p_3 h_3} Y_{p_3 h_3}^{J_3 i} C_{p_3 h_3}^\dagger (\overline{J_3 M_3}) |HF\rangle.
\end{aligned} \tag{20}$$

To perform this derivation we use the exact commutator between particle-hole pair creation and annihilation operators

$$\begin{aligned}
& [C_{p_1 h_1} (J_1 M_1), C_{p_2 h_2}^\dagger (J_2 M_2)] = \delta_{p_1 p_2} \delta_{h_1 h_2} \delta_{J_1 J_2} \delta_{M_1 M_2} \\
& - \underbrace{\sum_{\sigma_1 \sigma'_1 \sigma_2 \sigma'_2} \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | J_1 M_1 \rangle \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_2 | J_2 M_2 \rangle \left(\delta_{p_1 p_2} \delta_{\sigma_1 \sigma_2} a_{h_2 \sigma'_2}^\dagger a_{h_1 \sigma'_1} + \delta_{h_1 h_2} \delta_{\sigma'_1 \sigma'_2} a_{p_2 \sigma_2}^\dagger a_{p_1 \sigma_1} \right)}_{\text{Pauli correction}}.
\end{aligned} \tag{21}$$

The commutator (21) deserves special discussion. If we kept only the first term in r.h.s (21), this would correspond to standard RPA quasiboson approximation. The Pauli correction part is roughly proportional to the total number of particle and hole excitations in the RPA state, that means the more the RPA ground state deviates from the Hartree-Fock Slater determinant, the larger the Pauli corrections contribution to the r.h.s of the commutator (21) become and the more pronounced deviation from the bosonic behaviour of operators $C^\dagger(C)$ we see.

Coming back to (20) and taking into account that $|HF\rangle$ is vacuum for the Hartree-Fock quasiparticle operators, after some straightforward algebra we transform (20) to the following form:

$$\sum_{p' h'} T_{p h p' h'}^J X_{p' h'}^{J_i} - \underbrace{\sum_{p' h' J'} T_{p h p' h'}^{J'} W(J', J) X_{p' h'}^{J_i}}_{\text{Pauli correction}} = Y_{p h}^{J_i}. \tag{22}$$

Here matrix W is

$$\begin{aligned}
W(J', J) &= \sum_{M'=-J'}^{J'} \sum_{\sigma_1 \sigma'_1 \sigma_2 \sigma'_2} (-1)^{J+J'+M+M'} \\
&\times \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_1 | JM \rangle \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | J' M' \rangle \\
&\times \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_2 | J' - M' \rangle \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_2 | J - M \rangle.
\end{aligned} \tag{23}$$

Matrix W (23) is calculated numerically by summing up the corresponding Clebsch-Gordan coefficients and it is

$$W(0, 0) = \frac{1}{2}, \quad W(0, 1) = -\frac{1}{2}, \tag{24}$$

$$W(1, 0) = -\frac{3}{2}, \quad W(1, 1) = -\frac{1}{2}. \tag{25}$$

The similar to (22) equation was obtained to describe RPA ground state correlations in spherical nuclei by Lenske and Wambach.¹⁸

B. Calculation single-particle density matrices

Many molecular observables can be expressed in terms of single-particle density matrix. We define single-particle density matrix operators as

$$\rho_{p'p} = \sum_{\sigma} a_{p\sigma}^\dagger a_{p'\sigma}, \quad \rho_{h'h} = \sum_{\sigma} a_{p\sigma}^\dagger a_{p'\sigma}. \tag{26}$$

We show detailed derivation of the expectation value for operator $\rho_{p'p}$ in the RPA ground state. The calculations for $\rho_{h'h}$ are almost identical, we simply write the final expression for its expectation value in the end of the derivations.

We begin with the calculations of two commutators

$$[\rho_{p'p}, C_{p_1 h_1}^\dagger (JM)] = \delta_{p'p_1} C_{p h_1}^\dagger (JM), \tag{27}$$

$$[\rho_{p'p}, S] = \sum_{JM} \sum_{h_1 p_2 h_2} T_{p' h_1 p_2 h_2}^J C_{p h_1}^\dagger (JM) C_{p_2 h_2}^\dagger (\overline{JM}). \tag{28}$$

The expectation value is

$$\begin{aligned}
\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle &= \langle \Psi_0 | \rho_{p'p} e^S | HF \rangle = \\
\langle \Psi_0 | e^S \left(\rho_{p'p} + [\rho_{p'p}, S] + \frac{1}{2} [[\rho_{p'p}, S], S] + \dots \right) | HF \rangle
\end{aligned}$$

Taking into account that $\rho_{p'p} |HF\rangle = 0$ (since $|HF\rangle$ is vacuum for Hartree-Fock annihilation operators) and that $[[\rho_{p'p}, S], S] = 0$ (since $[\rho_{p'p}, S] \sim C^\dagger$) so that it and all higher terms vanish, we get

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \langle \Psi_0 | e^S [\rho_{p'p}, S] | HF \rangle. \tag{29}$$

Then, again, since the commutator $[\rho_{p'p}, S]$ commutes with S , the expectation value becomes

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \langle \Psi_0 | [\rho_{p'p}, S] | \Psi_0 \rangle. \tag{30}$$

Substituting the commutator (28) into (30) we get

$$\begin{aligned} \langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = & \quad (31) \\ \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_1 p_2 h_2}^J \langle \Psi_0 | C_{ph_1}^\dagger(JM) C_{p_2 h_2}^\dagger(\overline{JM}) | \Psi_0 \rangle. \end{aligned}$$

We express $C_{p_2 h_2}^\dagger(\overline{JM})$ in terms of RPA excitation and

annihilation operators

$$C_{p_2 h_2}^\dagger(\overline{JM}) = \sum_i X_{p_2 h_2}^{Ji} Q_{JM i}^\dagger + Y_{p_2 h_2}^{Ji} Q_{JM i} \quad (32)$$

and substitute it back into the equation (31):

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \sum_i \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_1 p_2 h_2}^J X_{p_2 h_2}^{Ji} \langle \Psi_0 | C_{ph_1}^\dagger(JM) Q_{JM i}^\dagger | \Psi_0 \rangle.$$

Contracting the amplitude X and coefficient T with the use of equation (22), we get

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \sum_i \sum_{JM} \sum_{h_1} \left(Y_{p'h_1}^{Ji} + \sum_{p_3 h_3 J_1} T_{p'h_3 p_3 h_1}^{J_1} W(J_1, J) X_{p_3 h_3}^{Ji} \right) \langle \Psi_0 | C_{ph_1}^\dagger(JM) Q_{JM i}^\dagger | \Psi_0 \rangle. \quad (33)$$

The calculation of the first term in (33) is straightforward

$$\begin{aligned} & \sum_i \sum_{JM} \sum_{h_1} Y_{p'h_1}^{Ji} \langle \Psi_0 | C_{ph_1}^\dagger(JM) Q_{JM i}^\dagger | \Psi_0 \rangle \\ &= \sum_{ii'} \sum_{JM} \sum_{h_1} Y_{p'h_1}^{Ji} Y_{ph_1}^{Ji'} \underbrace{\langle \Psi_0 | Q_{JM i'} Q_{JM i}^\dagger | \Psi_0 \rangle}_{\delta_{ii'}} \\ &= \sum_i \sum_{JM} \sum_{h_1} Y_{p'h_1}^{Ji} Y_{ph_1}^{Ji} \end{aligned} \quad (34)$$

The calculation of the second term in (33) is more involved and will be given in some details in the appendix. The result is very interesting: The second term in (33), that is the Pauli principle corrections to the expectation value of single particle density matrix $\rho_{p'p}$, is the expectation value of the density matrix itself taken with negative sign:

$$\sum_{J_1} \sum_i \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) X_{p_2 h_2}^{Ji} \langle \Psi_0 | C_{ph_1}^\dagger(JM) Q_{JM i}^\dagger | \Psi_0 \rangle = - \langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle \quad (35)$$

Combining these two terms (34,35) together into (33) we get

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \sum_i \sum_{JM} \sum_h Y_{p'h}^{Ji} Y_{ph}^{Ji} - \underbrace{\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle}_{\text{Pauli correction}}, \quad (36)$$

which means

$$\langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle = \underbrace{\frac{1}{2}}_{\text{Pauli correction}} \sum_i \sum_{JM} \sum_h Y_{p'h}^{Ji} Y_{ph}^{Ji}. \quad (37)$$

The similar calculations is performed for single-particle density matrix for occupied molecular orbitals with the result

$$\langle \Psi_0 | \rho_{h'h} | \Psi_0 \rangle = \underbrace{\frac{1}{2}}_{\text{Pauli correction}} \sum_i \sum_{JM} \sum_p Y_{ph'}^{Ji} Y_{ph}^{Ji}. \quad (38)$$

III. TEST RESULTS

We illustrate the role of the Pauli principle violation in the RPA ground state by the calculation of molecular dipole moments. A dipole moment is one the best observable for our purposes since it is directly related to the single-particle density matrices and it has readily available accurate experimental values for many molecules.

Let us consider dipole moment operator written in the second quantised form

$$d = \sum_{\sigma} \sum_{kl} \langle k | d | l \rangle c_{k\sigma}^\dagger c_{l\sigma}, \quad (39)$$

where $\langle k | d | l \rangle$ is the matrix element of dipole moment between Hartree-Fock orbitals. Transforming it to Hartree-

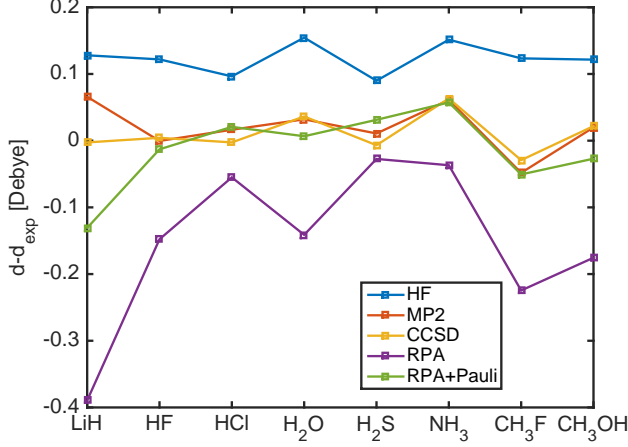


FIG. 1: Difference between computed and experimental values of the dipole moments. The experimental values of the dipole moments are taken from NIST Computational Chemistry Comparison and Benchmark Database²².

Fock quasiparticle basis (3,4), we get

$$d = 2 \sum_h \langle h|d|h \rangle + \sum_{pp'} \langle p|d|p' \rangle \rho_{p'p} - \sum_{hh'} \langle h|d|h' \rangle \rho_{h'h}. \quad (40)$$

Here the first term is the Hartree-Fock value for the molecular dipole moment. We omit in (40) terms proportional to $a_{p\sigma}^\dagger a_{h\sigma}^\dagger$ and $a_{h\sigma} a_{p\sigma}$. These terms are linearly proportional to $C_{ph}^\dagger(JM)$ and $C_{ph}(JM)$, respectively, therefore they are also linear in excitation creation Q_{JM}^\dagger and annihilation operators Q_{JM} and do not contribute to RPA ground state expectation value due to (10).

Using the expressions obtained in the previous section for single particle density matrices in the RPA ground state, we obtain the following equation for the molecular dipole moment

$$\begin{aligned} \langle \Psi_0 | d | \Psi_0 \rangle &= 2 \sum_h \langle h|d|h \rangle \\ &+ \frac{1}{2} \sum_i \sum_{JM} \left(\sum_{h'p'} \langle p|d|p' \rangle Y_{p'h}^{Ji} Y_{ph}^{Ji} \right. \\ &\quad \left. - \sum_{h'p'} \langle h|d|h' \rangle Y_{ph'}^{Ji} Y_{ph}^{Ji} \right). \end{aligned} \quad (41)$$

The extra factor 1/2 originates from the restoration of the Pauli principle in the RPA ground state.

We compute molecular dipole moments for a representative set of molecules (lithium hydride, hydrogen fluoride, hydrogen chloride, water, hydrogen sulfide, am-

monia, methyl fluoride, and methanol). All calculations have been performed with a development version of Mendelev computer program for *ab initio* quantum chemical calculations.²³ The current RPA implementation uses Hartree-Fock reference molecular orbitals and the details of the numerical implementation of RPA method is described in.²⁴ The results of RPA with the Pauli principle correction are compared with the standard RPA approach as well as with the Hartree-Fock (HF), Møller-Plesset second order perturbation theory (MP2) and coupled-cluster singles and doubles method (CCSD). We used 6-311++G(3df,3pd) basis set (cartesian form) in all calculations. The molecular geometries are taken from NIST Computational Chemistry Comparison and Benchmark Database²². The computed values are also assessed against the experimental results.

The results of the calculations is summarised in Fig.1. As seen in Fig.1, Hartree-Fock theory systematically overestimated molecular dipole moments. The RPA (without the correction for the violation of the Pauli principle) produces too strongly correlated electronic ground states, which lowers the value of the dipole moment well below the experimental results. Restoring the Pauli principle in the RPA ground state (RPA+Pauli curve in Fig.1) brings the computed value close to the experimental data and gives accuracy on a par with MP2 and CCSD methods.

IV. DISCUSSIONS AND CONCLUSIONS

One of the main results of the paper are equations (22) and (36). Eq.(22) determines the operator S in the RPA ground state $e^S|HF\rangle$ taking into account exact commutation relations between particle-hole pair excitation operators (21) that means the full account of the Pauli principle in the construction of the ground state wavefunction. The addition Pauli correction term in (22) leads to the extra term in the single particle density matrix. The Pauli principle correction to the single particle density matrix is the same density matrix itself taken with the negative sign, see (36). The result of proper consideration of the Pauli principle leads to the extra $\frac{1}{2}$ factor in the expressions for molecular observables (37,41).

This extra $\frac{1}{2}$ has the same physical nature as additional $\frac{1}{2}$ factor in the RPA with exchange total ground state energy where it was rigorously justified via anti-symmetrisation of fluctuation potential operator.¹ We think that the effective Lagrangian method^{25,26} yields correct extra factor $\frac{1}{2}$ for single-particle molecular observables if the corresponding effective Lagrangian is defined with the use of the RPA total energy with correct extra anti-symmetrisation factor - although it is yet to be demonstrated rigorously.

The comparison with ring coupled cluster doubles (ring-CCD) ground state brings an interesting puzzle. RPA expression (7) for ground state is the same as CCD wavefunction,¹⁵ and ring-CCD defines the coefficient T as

$\mathbf{T} = \mathbf{X}^{-1}\mathbf{Y}$, which is apparently the RPA equation for T without Pauli corrections (compare eq.(13a) in¹⁵ with equation (22) in this paper). At the same time ring-CCD yields correct extra factor $\frac{1}{2}$ in the final formula for the ground state correlated energy.¹⁵

To summarise, we develop a theoretical method to restore the Pauli exclusion principle in the RPA correlated wavefunction. We obtained new, corrected for the Pauli principle expression for the RPA ground state correlated wavefunction. The method is *a posteriori* approach: The RPA eigenvalue problem remains intact and only the final expressions for molecular observables are corrected by $\frac{1}{2}$ factor. The role of proposed Pauli principle corrections is illustrated by the calculations of molecular dipole moments. The corrected for the Pauli principle RPA ground

gives results of comparable accuracy with Møller-Plesset second order perturbation theory and coupled-cluster singles and doubles method, while standard RPA significantly overcount the role electronic correlations.

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Appendix A: Derivation of eq.(35)

$$\begin{aligned}
& \sum_{J_1} \sum_i \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) X_{p_2 h_2}^{J_i} \langle \Psi_0 | C_{p h_1}^\dagger (JM) Q_{JM}^\dagger | \Psi_0 \rangle \\
&= \sum_{J_1} \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) \langle \Psi_0 | C_{p h_1}^\dagger (JM) C_{p_2 h_2}^\dagger (\overline{JM}) | \Psi_0 \rangle \\
&= \sum_{J_1} \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) \sum_{\sigma_1 \sigma'_1 \sigma_2 \sigma'_2} \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | JM \rangle \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_2 | J - M \rangle (-1)^{J+M} \langle \Psi_0 | a_{p\sigma_1}^\dagger a_{h_1\sigma'_1}^\dagger a_{p_2\sigma_2}^\dagger a_{h_2\sigma'_2}^\dagger | \Psi_0 \rangle \\
&= - \sum_{J_1} \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) \sum_{\sigma_1 \sigma'_1 \sigma_2 \sigma'_2} \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | JM \rangle \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_2 | J - M \rangle (-1)^{J+M} \langle \Psi_0 | a_{p\sigma_1}^\dagger a_{h_2\sigma'_2}^\dagger a_{p_2\sigma_2}^\dagger a_{h_1\sigma'_1}^\dagger | \Psi_0 \rangle \\
&= - \sum_{J_1} \sum_{JM} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} W(J_1, J) \sum_{\sigma_1 \sigma'_1 \sigma_2 \sigma'_2} \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_1 | JM \rangle \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_2 | J - M \rangle (-1)^{J+M} \\
&\quad \times \sum_{J_2 M_2} \sum_{J_3 M_3} \langle \frac{1}{2} \sigma_1 \frac{1}{2} \sigma'_2 | J_2 M_2 \rangle \langle \frac{1}{2} \sigma_2 \frac{1}{2} \sigma'_1 | J_3 - M_3 \rangle (-1)^{J_3+M_3} \underbrace{\langle \Psi_0 | C_{p h_2}^\dagger (J_2 M_2) C_{p_2 h_1}^\dagger (\overline{J_3 M_3}) | \Psi_0 \rangle}_{\sim \delta_{J_2 J_3} \delta_{M_2 M_3}} \\
&= - \sum_{J_1} \sum_{J_2 M_2} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} \underbrace{\sum_J W(J_1, J) W(J, J_2)}_{\delta_{J_1 J_2}} \langle \Psi_0 | C_{p h_1}^\dagger (J_2 M_2) C_{p_2 h_2}^\dagger (\overline{J_2 M_2}) | \Psi_0 \rangle \\
&= - \sum_{J_2 M_2} \sum_{h_1 p_2 h_2} T_{p'h_2 p_2 h_1}^{J_1} \langle \Psi_0 | C_{p h_1}^\dagger (J_2 M_2) C_{p_2 h_2}^\dagger (\overline{J_2 M_2}) | \Psi_0 \rangle = - \langle \Psi_0 | \rho_{p'p} | \Psi_0 \rangle
\end{aligned}$$

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